Ω **Metrohm**

Determination of TAN in engine oil with 859 Titrotherm

Of interest to: oil industry

Summary

The oil is dissolved in a mixture of toluene and 2-propanol (1:1) and titrated with standardized c(TBAOH) = 0.1 mol/L in 2-propanol/methanol to a catalytically determined thermometric endpoint.

Introduction

In a titration, the titrant reacts with the analyte in the sample either exothermically (gives out heat) or endo-thermically (takes in heat). The Thermoprobe meas-ures the temperature of the titrating solution. When all of the analyte in the sample has reacted with the titrant, the temperature of the solution will change, and the endpoint of the titration is revealed by an inflection in the temperature curve.

Catalytically enhanced titrations using paraformalde-hyde as catalyst are based on the endothermic hydro-lysis of the paraformaldehyde in the presence of excess hydroxide ions.

The amount of analyte determined is not related to the change in temperature of the solution. Therefore, it is not necessary to use isulated titration vessels.

Theory

Thermometric titrations are conducted under condi-tions of constant titrant addition rate. In this respect they differ from potentiometric titrations, where the titrant addition rate may be varied during the titration according to the electrode response. In thermometric titrations, a constant addition rate of titrant equates to a constant amount of heat being given out or con-sumed, and hence a more or less constant tempera-ture change up to the endpoint.

Apparatus and accessories

1 x 2.859.1010	859 Titrotherm (1 Dosino and 1 10 mL Dosing unit included)	
2 x 2.800.0010	800 Dosino	
1 x 6.3032.120	Dosing unit 2 mL	
1 x 6.3032.250	Dosing unit 50 mL	
1 x 6.1543.210	3-way stopper with antidiffusion tip	
1 x 6.1446.000	3 x SGJ stoppers	
1 x 6.2061.010	Reagent organizer	
1 x 6.2065.000	Stacking frame	

Reagents

Titrant: c(TBAOH) = 0.1 mol/L in 2-propanol/methanol (Merck)
Solvent mixture: Toluene 99% (Fluka)/2-propanol purum (Fluka) 1:1 (v/v)
Catalyst: Paraformaldehyde, 95% (Fluka)
Standard solution: 0.1 mol/L standardized benzoic acid in 2-propanol (puriss. p.a., Fluka)

Sample

Used engine oil "Turbo 254"

Calculations

Titer TBAOH with 0.1 mol/L benzoic acid solution

If a liquid primary standard is used, dose aliquots directly into the titration vessel. Set up a regression plot with the sample size in mL on the x-axis and mL of titrant consumed on the y-axis. The plot will be a linear curve of the form $y = a * x + b$, where the molar-ity of the titrant is calculated from the slope (a) with the following formula:

$(slope)^{-1}$ * c(standard solution)

Calculation of titer in tiamo™

Assignment	RS name	Formula
RS01	EP	TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR'*'RS.EP.COR'
RS05	Molarity[mol/L] of titrant	(1/'RS.EP.SLO')*'benzoic acid. CONC'
RS06	Titer of titrant	(1/'RS.EP.SLO')*'benzoic acid. CONC/'TET1'.CONC'
RS07	Filter factor	'MV.filter factor'

method blank

The method blank is determined by titrating a number of analyte solutions of different concentrations and plotting the analyte concentration against the titrant consumption. The method blank is determined as the y-intercept from a linear regression of the titration data. Changes in method parameters will require a new determination of method blank.

This parameter is stored along with the other method parameters. For all determinations it is subtracted from the volume of titrant.

Calculation of method blank in tiamo™

Assignment	RS name	Formula
RS01	EP	TET1.EP(1).VOL'
RS02	Slope	'RS.EP.SLO'
RS03	Intercept [mL]	'RS.EP.ITC'
RS04	Correlation (R^2)	'RS.EP.COR'*'RS.EP.COR'
RS07	Filter factor	'MV.filter factor'

Calculation of TAN determination in tiamo™

Assignment	RS name	Formula
RS01	EP	TET1.EP(1).VOL'
RS07	Filter factor	'MV.filter factor'
RS08	TAN mg KOH/g	('TET1.EP(1).VOL'-'CV.blank')*'TET1.CONC'*'TET1.TITER'*MW.KOH'/'MV.sample size
RS09	Blank [mL]	'CV.blank'

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Legend formula

'TET1.EP(1).VOL'	= Thermometric titration end point volume
'RS.EP.SLO'	= slope for linear regression
'RS.EP.ITC'	= Intercept for linear regression
'RS.EP.COR*'RS.EP.COR'	= correlation coefficient (R^2)
'MV.filter factor'	= Titration parameter (smoothing factor)
CV.blank'	= method blank in mL
'bencoic acid'.CONC'	= Concentration of standard solution (0.1 mol/L)
'TET1.CONC'	= Concentration of the titrant (0.1 mol/L)
'TET1.TITER'	= titer of the titrant
'MV.sample size'	= sample size in g
TAN mg KOH/g	= total acid number in mg KOH/g
'MW.KOH'	= 56.10564 g/mol

Sample preparation for titer, blank and sample

	Titer determination	Blank determination	Sample determination
Benzoic acid 0.1 mol/L [mL]	1 - 5	-	-
Toluene/2-propanol 1:1 (v/v) [mL]	35	35	35
engine oil [g]	-	0.13 – 0.40*	0.25 – 0.28*
number of determination (n =)	3 - 5	3 - 5	3 - 5

*depends on sample type

Expected TAN mg KOH/g sample	Sample weight in g	Weighing accuracy in mg
0.05 … 0.9	10 ± 2	100
1 … 4.9	5 ± 0.5	20
5 … 19	1 ± 0.1	5
20 … 99	**0.25 ± 0.02**	1
100 … 250	0.1 ± 0.01	0.5

Method

Procedure for titer determination

Give approx. 0.5 g paraformaldehyde into the titration vessel, add an aliquote of standardized benzoic acid solution and 35 mL solvent mixture. Stir thoroughly for 20 seconds before titration. Titrate at least 3 different values of benzoic acid in an ascending order to the first exothermic endpoint. With the formula "Calculation of titer in *tiamo*TM" the titer is automatically calculated.

Procedure for method blank determination

The method blank is determination by titrating a range of aliquot sizes, and calculating the y-intercept (in mL) of a regression curve formed by plotting aliquote size

(x-axis) against mL of titrant delivery (y-axis). This can be done automatically in *tiamo*TM.
Pipette an aliquote of oil (see "Sample preparation for titer, blank and sample") directly into the titration vessel, add approximately 0.5 - 0.7 g paraformaldehyde and 35 mL solvent mixture. Stir thoroughly for 30 seconds and titrate to a single thermometric endpoint. The method blank is automatically calculated with the formula "Calculation of method blank in *tiamo*TM". The intercept in mL, which represents the method blank, will be saved as a common variable. This blank has to be subtracted from each further analyzed sample.

Titration Parameters for engine oil

	Titer determination	Blank determination	engine oil
Stirring rate	5	15	15
Start volume [mL]	0	0	0
Pause [s]	20	30	30
Switch off autom.	yes	yes	yes
Dosing rate [mL/min]	7	4	4
Filter factor	60	60	60
Damping until [mL]	1.0	0	0
Stop volume [mL]	6	1.5	2
Stop slope	off	off	off
Add. volume after stop [mL]	0.5	0.5	0.5
Evaluation start [mL]	0	0	0
End points [Reaction type]	ex*	ex*	ex*
EP criterion [ERC]	-2	-10	-10

* exothermic

Procedure for sample preparation

Pipette an aliquote of oil (see "Sample preparation for titer, blank and sample") directly into the titration vessel, add approximately 0.5 - 0.7 g paraformaldehyde and 35 mL solvent mixture and titrate to a single thermometric endpoint. The TAN value in mg KOH/g is automatically calculated with the formula "Calculation of TAN determination in *tiamo*™".

## Linear regression of blank engine oil (method blank = 0.0638 mL)
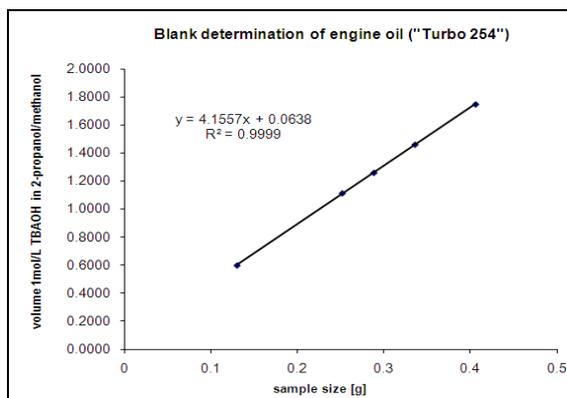
Results (titer and blank)

	Titer TBAOH	Blank engine oil
endpoint [mL]	4.9933	1.7467
slope	0.9987	4.1557
intercept [mL]	0.1213	0.0638
Correlation (R^2)	1.0000	0.9999
molarity [mol/L]	0.1001	-
Filter factor	60	60
titer	1.001	-

Result of used engine oil sample "Turbo 254"

	engine oil
TAN mg KOH/g	22.85
s(abs) mg KOH/g	0.06
s(rel) %	0.26
n =	5

Thermometric Titration Plot (engine oil)
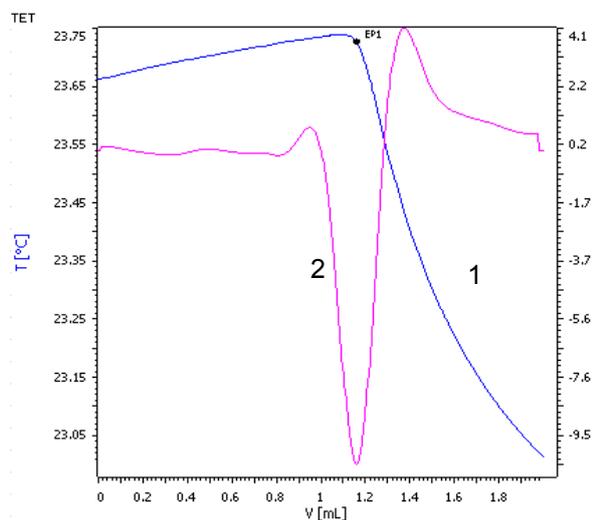
Legend:

1   = solution temperature curve

2   = second derivative curve (for endpoints)